A NAFION IONOMER / CONJUGATED IONIC POLYACETYLENE MATRIX COMPOSITE

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Abstract

Polymer matrix composites are prepared by incorporating a highly conjugated substituted polyacetylene into a Nafion ionomer membrane. The monomer, 2-ethynylpyridine (2EP) is quaternized within the ionic domains of Nafion. An in-situ polymerization occurs upon heating the membranes which contain 5-15% by weight of 2EP. Dynamic mechanical analysis and thermogravimetric analysis studies indicate that the mechanical properties and thermal stability of the composites are superior to Nafion. Gas permeability coefficients of O_2 and N_2 are measured. Preliminary results indicate significant increase in the separation factor ($\alpha = PeO_2/PeN_2$) within the composite.

Introduction

Preparation and characterization of novel microcomposite membranes containing Nafion and a highly conjugated substituted ionic polyacetylene have been reported. (1) Nafion is a perfluorocarbonsulfonic acid with sulfonic groups bound to fluoroether side chains as shown in Figure 1. The morphology is characterized by microphase separation between the hydrophobic fluorocarbon and the hydrophilic domains, the latter forming a "cluster-channel" network. The clusters in dry Nafion are approximately 5nm in size and connected by channels of 1nm in diameter. (2)

The 2EP used in this study has been studied with its trimethylsily derivative to polymerize a novel family of highly conjugated ionic polyacetylenes. (3) The triple bond is activated via quaternization of the pyridine nitrogen with methyl trifluoromethane sulfonate (triflate). The polymerization of N-methylethynylpyridinium salt is shown in Figure 2.

In Nafion, the sulfonic acid side groups can quaternize 2EP molecules introduced into the membrane. A polysalt of 2EP monomer forms in the cluster-channel regions which function as microreactors for subsequent thermal polymerization. The microcomposites contain up to 15% by weight of acetylene monomer.

In this study, we are interested in the mechanical properties and gas permeation behavior of these membranes. Since Nafion has good thermal, mechanical and chemical properties (4,5) and substituted polyacetylenes have excellent permeation properties, (6,7,8) these microcomposites membranes may be of interest for permeation applications.

Experimental

Details of sample preparation are described in (1). Results are given below, for membranes of C1 and C4 series obtained by immersing a dry pretreated Nafion in a 2EP bath and series C2 and C3 are obtained by immersing a water-boiled Nafion in a 2EP bath. The 2EP content is listed in Table 1-3. Although some polymerization is detected at room temperature, polymerization is completed by heating the sample at 200°C under N_2 for 10 minutes.

Stress-strain measurements were performed at room temperature using a Chatillon TCD 500 tensile test machine. The following parameters were used: crosshead speed: 2 in/min; length: 2.54 cm; sample size: 0.0175 x 0.5 x 4 cm^3.

Dynamic mechanical measurements were performed with a Seiko DMS-200 instrument. The samples were under nitrogen in the dynamic mechanical analysis (DMA) chamber and were run at 4°C/minute at 1 Hz from -150 to 250°C. The storage loss modulus, E', the loss modulus, E", were recorded as a function of temperature. Samples were cooled using liquid nitrogen and the auto-cooling accessory.

Gas permeation experiments were carried out at 32, 42 and 52°C for nitrogen and oxygen gases. A Custom Scientific CS-135 permeation cell was used for the experiments at a constant pressure of 14.7 psi.

The DMA data of $\tan\delta$ as a function of temperature for Nafion and the composite membranes are found in Figure 3. Three peaks, α, β and γ, are assigned as the glass transition temperature, the ionic cluster transition, and the local chain motion of the matrix polymer, respectively. The glass transition temperature and the ionic cluster transition are increased by approximately 150 and 100°C respectively upon introducing 2EP into the ionic regions of the Nafion matrix. This is attributed to the strong ionic interactions between the sulfonate and pyridinium moieties. Similar behavior has been reported for Nafion which is neutralized with a metal ion such as lithium or sodium.(9,10,11)

Nafion is flexible with an elongation of 2.4 and Young's modulus of 45.5 MPa as shown in Figure 4 and Table 1. However, as 2EP is incorporated into the membrane, the mechanical properties of Nafion change. For example, upon incorporating 15.5% of 2EP into the Nafion membrane, the membrane becomes brittle and Young's modulus is 1143 MPa. This type of ductile-brittle transition has also been reported in silicon oxide filled Nafion membrane.(12)

Mechanical properties are not significantly changed by heat treatment of membranes, suggesting that they are primarily determined by the introduction of 2-ethynylpyridinium counterion within the ionic domains. In the DMA data, as shown in Figure 5, the ionic cluster transition is not visible for the heated sample and this could be attributed to the polymerization which restrains motion within the ionic cluster. There is the possibility that it has shifted to higher temperature and occurs under the broad glass transition peak.

The E' data on the first and second heat DMA scans suggest that there is no shrinkage of the samples. This is perhaps because ionic crosslinks have formed between the polyacetylene and Nafion suggesting high free volume which is important for permeation applications.

The gas permeation data for the Nafion and composite membranes at 32°C are found in Table 2. The permeation coefficients (Pe) for both nitrogen and oxygen decrease with increasing 2EP content within the membrane. This effect is especially pronounced for oxygen permeation. The separation faction ($\alpha = O2/N2$) of the membrane containing 5% 2EP has a value of 6 compared to 2 for pure Nafion. This may be explained by the oxygen affinity of substituted polyacetylenes.(6).

within the ionic regions dramatically affects the permselectivity. Table 2 shows Pe values for a membrane containing 15 % by weight 2EP before and after polymerization by heating the sample. Pe(N_2) is dramatically decreased (and could not be detected), while Pe(O_2) decreased only slightly.

Table 3 contains permeation data as a function of temperature. The results show for a membrane which contains 15% 2EP, the Pe for both nitrogen and oxygen increases with temperature while the permselectivity is decreased. Similar behavior has been observed for substituted polyacetylene membranes.(6)

The activation energies, 24.7 and 40.8 kcal/mol have been calculated for the microcomposite membranes for oxygen and nitrogen gas respectively. In comparison with reported results for substituted polyacetylene, the values are one order of magnitude higher. (6)

Several research groups have found that the Pe for polyacetylenes decreases by two orders of magnitude as a function time (7,8) upon aging of the membrane. This is contrary to the microcomposite membranes in this study. The membranes are stable with time and this is again attributed to the ionic crosslinking and interpenetrating network which prevents relaxation of the polymer chain. The free volume is retained and can help contribute to an increased Pe.

These exploratory permeation studies are still in progress to study further the Nafion / 2EP membrane which contains 5% 2EP monomer and has a permselectivity in the range of 4.5 to 6. These values, together with the mechanical properties and thermal stability, provide an interesting membrane candidate for an oxygen enrichment membrane for a variety of medical and engineering applications.

Acknowledgments

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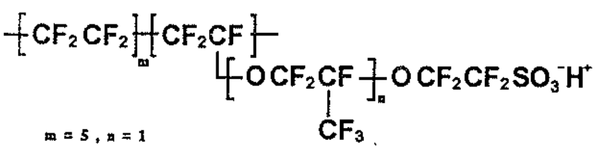


Figure 1. Chemical structure of Nafion.

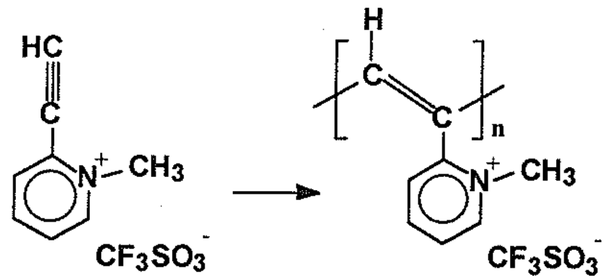


Figure 2. Chemical structure of N-methylethynyl-pyridinium triflate salt and polymerization product.

Figure 3. Dynamic mechanical analysis data , tanδ and E' of 1) Pretreated Nafion and 2) a 2EP/Nafion composite containing 13.3wt% 2EP, First heating

Figure 4. Stress-Strain curves of 2EP/Nafion composite membranes.

Table 1. Mechanical properties of 2EP/Nafion composite membranes.

Sample	2EP content (wt%)	Strain at break (ΔL/L)	Stress at break (MPa)	Young's Modulus (MPa)
Nafion	0	2.4	35.5	45.48
C2	15.5	0.06	69.9	1143
C4[a]	5.5	0.8	27.1	84.38
C4[b]	2.7	1.1	32.4	99

[a] before heating.
[b] after heating to 200°C for 10 min.

Figure 5. Dynamic Mechanical analysis data , tanδ and E' of 2EP/Nafion composite membrane 1)before and 2) after heating.

Table 2. Permeation behavior of 2EP/Nafion composite membranes.

Sample	PeO_2 x 10^{10} Barrer	PeN_2 x 10^{10} Barrer	α	2EP content (wt%)
Nafion	8.44	4.14	2.04	0
C1	3.37	0.70	4.84	5
C4	3.11	0.49	6.41	5.5
C3[a]	0.95	0.30	3.18	15
C3[b]	0.70	ND	—	15

1 Barrer = 1 x 10^{-10} [cm^3 x cm]/[cm^2 x sec x cm-Hg]
ND = not detected

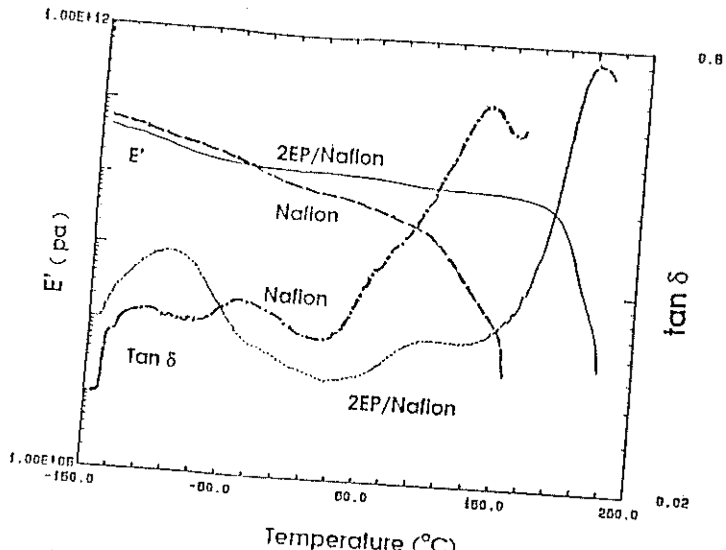
Table 3. Temperature effect on the permeation behavior of 2EP/Nafion membrane.

C3[a]	$PeO_2 x 10^{10}$ Barrer	$PeN_2 x 10^{10}$ Barrer	α
32°C	0.95	0.30	3.2
42°C	7.57	5.25	1.4
52°C	9.77	14.41	0.68

[a] before heating.

Key Word

polyacetylene, Nafion, microcomposite, permeation.



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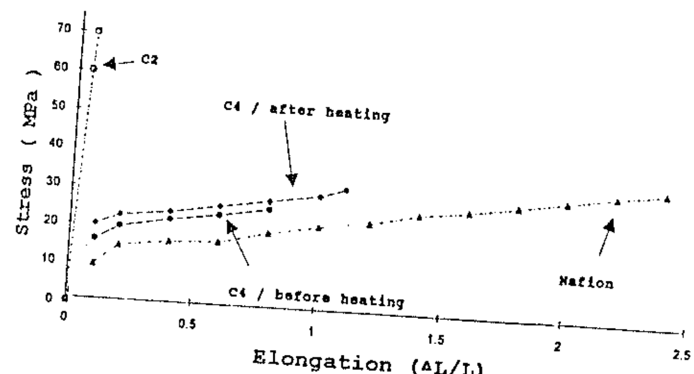

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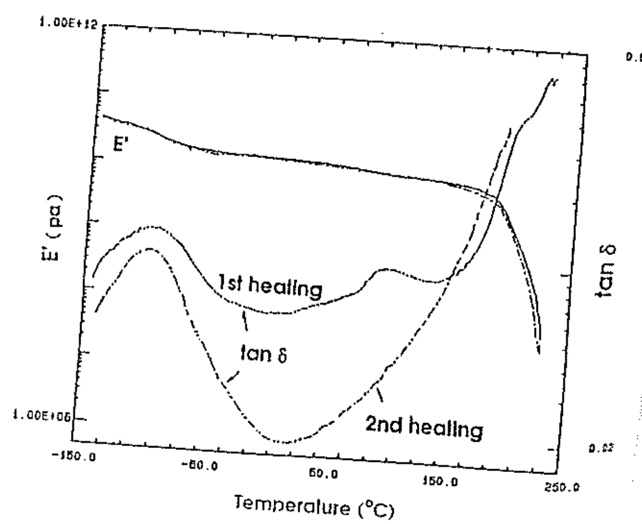

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